THERMAL CONDUCTIVITY OF CHALCOGENIDE As_2S_3 THIN FILMS

Sok Won Kim[2,4], Hyojung Yu[2], Chang Ho Kang[2], Sang Hyun Lee[3], Jong Chul Kim[3]

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[2] Department of Physics, University of Ulsan, Ulsan 680-749, Korea.

[3] Division of Physical Metrology, Korea Research Institute of Standards and Science, Taejon 305-600, Korea.

[4] To whom correspondence should be addressed. E-mail: sokkim@mail.ulsan.ac.kr

ABSTRACT

Photo-induced modifications in chalcogenide films include changes in density, hardness, rheological properties, chemical reactivity, electrical and optical properties, therefore the chalcogenide films have been extensively studied recently, partly as an interesting subject for fundamental research in the field of disordered solids and partly due to potential applications in opto-electronics such as photo-resists, optical memories, opto-electronic circuits, etc. However, the thermal properties were not widely investigated compared to the optical and electrical properties.

In this study, amorphous As_2S_3 thin film samples, whose thicknesses are 0.5 μm, 1.0 μm, 2.0 μm, and 4.0 μm, were prepared on silicon wafers by the thermal evaporation, and their thermal conductivity was measured by a 3ω method between room temperature and 100 °C. These measurements were repeated after the illumination of Ar^+ laser beam whose photon energy is consistent with the band energy gap of As_2S_3, and continued for the annealed films in 180 °C for one hour. The result shows that the thermal conductivities of fresh films were 0.14～0.27 $Wm^{-1}K^{-1}$, however increase to 0.28～0.47 $Wm^{-1}K^{-1}$ after the illumination of light on the sample and decrease 0.19～0.42 $Wm^{-1}K^{-1}$ by annealing of the sample. These changes were explained by the change of microstructure produced from the photo-darkening and thermal annealing.

KEY WORDS: arsenic tri-sulfide; chalcogenide; photo-darkening; thermal conductivity; thin film; three-omega method.

1. INTRODUCTION

The non-crystalline chalcogenides are solids without long-range order and, as a consequence, they are intrinsically metastable. These materials are susceptible to light-induced changes because they are characterized by intrinsic structural flexibility. The significant changes in the physical properties and structural modifications induced by light have been evidenced in many amorphous chalcogenide films [1-3]. Recent progress in the study of amorphous chalcogenide materials has led to increasing attention for the understanding of their structures and various properties at the microscopic level [4,5].

The photo-darkening, one of the various photo-induced effects that occur in these materials, is produced by the red shift of the optical band gap [6,7] and induces a large change in the optical [3], chemical [8], electrical [9], and thermal properties[10], however, compared to other properties, the thermal properties were not deeply and widely studied until now.

Among many chalcogenide materials, arsenic tri-sulfide (As_2S_3) is technically important because of its good transparency in the 0.7~11.0 μm wavelength range and excellent resistance against devitrification, moisture, and corrosion [11,12]. As_2S_3 exhibits a wide variety of photo-induced phenomena that enable it to be used as optical imaging or storage medium and recently, various electronic devices, including electro-optic information storage devices and optical mass memories [13]. Therefore the accurate measurement of thermal properties of As_2S_3 is necessary to study the memory density.

In this study, after the investigation of the light induced optical changes of amorphous As_2S_3 thin film samples coated on the slide glass, the same films with several thicknesses, were deposited on silicon wafers by the thermal evaporation, and their thermal conductivity was measured by a 3ω method. These measurements were repeated after the illumination of Ar^+ laser beam whose photon energy is consistent with the band energy gap of As_2S_3 and continued for the annealed films.

The 3ω method, one of the hot wire method, which can solve this problem is developed by David G. Cahill in 1987 [14]. This technique was developed to get the thermal conductivity of isotropic bulk materials whose thermal conductivity values are low, therefore it can be applied to the measurement of the thermal conductivity of low thermal conductivity thin films coated on the high thermal conductivity substrate such as silicon wafer [15].

2. THEORY

2.1. Photo-darkening of As_2S_3 thin films

When an As_2S_3 film was illuminated with band-gap light, the absorption band moves toward longer wavelength. We call this phenomenon as ″Photo-darkening″ because this means the strong absorption of the visible light and consequently the illuminated point becomes dark. The degree of this photo-darkening is dependent on the intensity of the light and begins to saturate from a certain intensity.

Several models were suggested for this photo-darkening, however the ″Defect Model″ and ″Double Well Potential Model″ seem to be appropriate. In accordance with

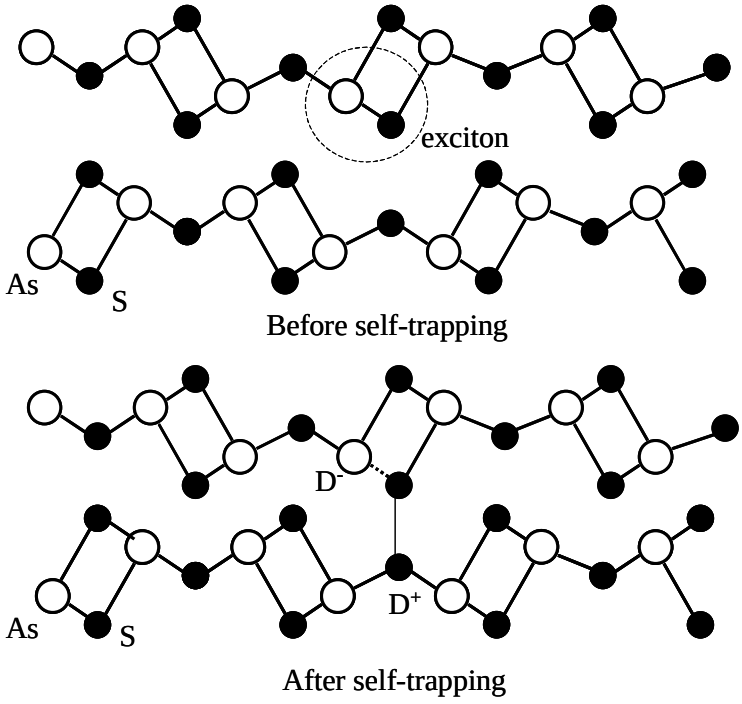


Fig. 1 Schematic of the transformation of an exciton in amorphous As_2S_3 into D^+ and D^- pairs accompanied by atomic distortion.

the defect model suggested by R. A. Street [16], when the amorphous As_2S_3 is illuminated by the band gap light, the lone-pair p electron of S-atom is excited and the exciton is produced as Fig. 1. This exciton is much unstable, therefore, returns to the original states or forms the defect pairs such as D^+ and D^-. When these defect pairs form, S (sulfur)-atom which has excess positive charge combines with the nearest S-atoms and becomes D^+ defect and vise versa. When these defect pairs produced, the microstructure changes locally, therefore the grain size changes and the absorption coefficient and refractive index increase. In order to restore to the original stable state which doesn't have any defects, the heat treatment such as annealing at the glass transition temperature is required.

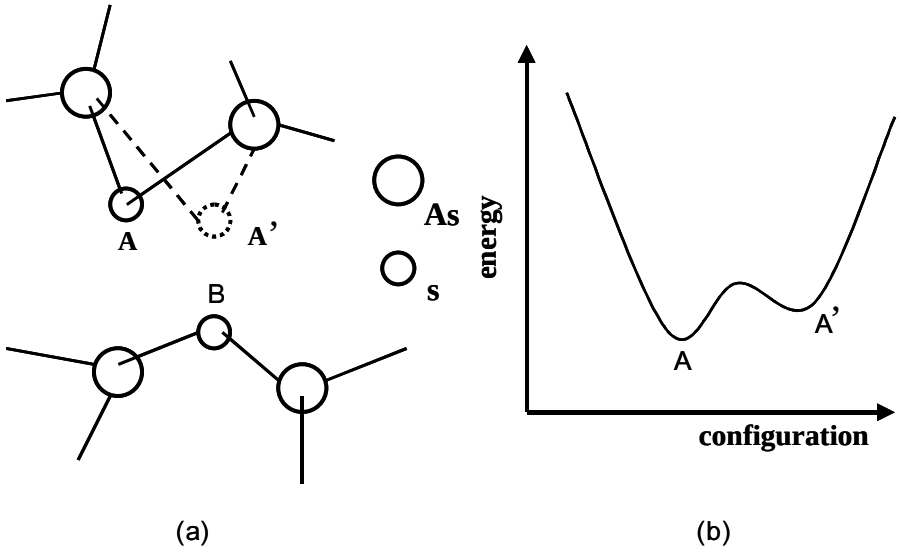


Fig. 2 Schematic model of (a) bistable local bonding geometries and (b) corresponding Double-Well-Potential.

K. Tanaka [6] suggested the double-well-potential model which treats the bending flexibility of the atoms. The A-A´ transition of atomic configuration shown in Fig. 2 involves implicitly not only a change in the distance between closed shells (A-B) but also a change in bond angle. Such a bending flexibility is strongly correlated with ionicity of chemical bond. Basically these two models are the same.

2.2. 3ω Method

The sample geometry is shown in Fig. 3. When an ac electric current of angular frequency ω is applied across the heater, it generates Joule heating at 2ω. Two pads are the connections for current and voltage leads. A gold strip is used as heater and thermometer simultaneously because it is not susceptible to oxidation and has suitable electrical resistivity.

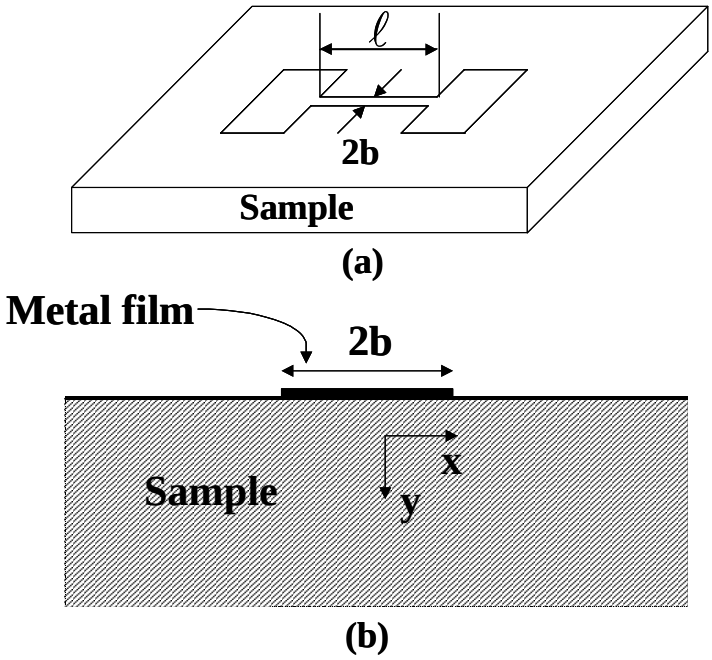


Fig.3 (a) Shape of prepared sample. Two pads are the connections for current leads and voltage leads. (b) Geometry of thermal diffusion structure. The full-width of metal line is 2b.

If the amplitude of sinusoidal heating is P, the temperature distribution in the substrate can be calculated as a superposition of temperature modulations by the infinitesimal line heaters. The solution given by Carslow and Jaeger [17] for the temperature modulation by a line heater of infinitesimally narrow width is proportional to $K_0(qr)$, where r is the distance from the heater, $K_0(x)$ is the modified Bessel function of zeroth order, and q is defined as [18]

$$q^2 = \frac{2i\omega C}{\kappa}, \tag{1}$$

where C and κ are the heat capacity and thermal conductivity of the sample, respectively. Integrating the solution by varying the position of infinitesimal heaters over the width of the flat heater, the temperature oscillation amplitude T_{ac} at the heater can be obtained in the Fourier k space as

$$T_{ac} = \frac{P}{l\pi\kappa}\int_0^\infty \frac{\sin^2(kb)dk}{(kb)^2\sqrt{k^2+q^2}.} \tag{2}$$

A geometrical effect of metal line as a thermal conductor is also neglected in order to get the relation in simpler form. The agreement between calculated and measured T_{ac} shows that this approximation seems to be valid. If the width of the heater is small enough to satisfy the condition $qb << 1$, Eq. (2) can be approximated by $\ln(qb) + const$. Also, if the heat capacity and thermal conductivity are both real values, q^2 becomes purely imaginary. Then, we can divide T_{ac} into real and imaginary parts to distinguish in-phase and out-of-phase oscillations of temperature as follows;

$$\frac{l\pi\kappa}{P}T_{ac} = -\ln(qb) + \eta = -\frac{1}{2}\ln\left(\frac{2\omega b^2 C}{\kappa}\right) + \eta - \frac{\pi}{4}i \tag{3}$$

where η is a constant.

Finally, thermal quantities can be calculated from $V_{3\omega}$-the measured rms value of 3ω voltages. The $V_{3\omega}(=V'_{3\omega}+iV'_{3\omega})$ is related with the temperature oscillation T_{ac} as

$$\begin{aligned} V_{3\omega} &= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} I(t)R(t)\cos(3\omega t)dt \\ &= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} 2I_0\cos\omega t\left[R + \frac{dR}{dT}T_{ac}\cos(2\omega t)\right]\cos(3\omega t)dt \\ &= \frac{I_0\alpha}{2}T_{ac}\,, \end{aligned} \tag{4}$$

where α is the temperature coefficient of the resistance R of the heater and I_0 is the rms value of the electric current along the heater generating a power of $P = I_0^2 R$. Equation (3) can be rewritten in terms of $V'_{3\omega}$ as

$$\kappa = -\frac{I_0^3 R\alpha}{4\pi\ell}\frac{d\ln\omega}{dV'_{3\omega}} \tag{5}$$

We consider now the case when a thin film with a lower thermal conductivity than the substrate is located between the substrate and the strip. The increase of temperature

oscillation of the film ΔT_f can be expressed in terms of a thermal conductivity of film κ_f [18]:

$$\Delta T_f = \frac{P\, t_f}{2b\, \kappa_f} \tag{6}$$

where t_f is the film thickness.

3. EXPERIMENTAL

3.1. Sample Preparation

The As_2S_3 film whose thickness is 1.0 μm was coated on the slide glass for the measurement of transmittance change induced by photo-darkening at first and after that, the films whose thickenesses are 0.5μm, 1.0 μm, 2.0 μm, and 4.0 μm, were coated on the silicon wafer for the measurement of thermal conductivity. All the films were coated in thermal evaporator and and the thickness was monitored by the crystal oscillator. During the deposition, the coating rate was fixed to 5 nm/s.

3.2 Experiment

In order to investigate the photo-darkening effect, the fresh film coated on glass was illuminated for 10 minutes with the 100 mW/cm^2 Ar^+ laser beam whose wavelength is 514.5 nm and photon energy (≈2.41 eV) is nearly consistent with the band energy gap of As_2S_3 (≈2.34 eV). The transmittance of the irradiated film and fresh film was measured by the spectrophotometer in the wavelength range of 400~800 nm.

As in Fig. 3, a narrow gold metal strip and the rectangular pads are evaporated onto the sample through a stainless steel mask and the lead lines are electrically connected to the pads. The samples mounted in the sample holder by epoxy and lead lines are connected to the pads using silver paste. Then, the metal strip is connected by four-probe type to the current and voltage lead lines, respectively. The width of the heater pattern is about 60 μm and its length is 4 mm.

The measurement circuit is shown in Fig. 4. Since the ω component of ac voltage at the heater causes a spurious signal at the lock-in amplifier, a Wheatstone bridge is used. R_1 and R_2 are fixed resistances, R_v and R_s are the rheostat resistance and resistance of the gold pattern, respectively. Since R_2 and R_v are a few tens of kΩ and R_1 and R_s are a few tens of Ω, most of the current flows through R_1 and R_s. In the experimental apparatus, to balance the bridge circuit, we adjusted the value of R_v to suppress the signal of ω and then to separate only the 3ω component of the voltage signal. In order to prevent rapid temperature variation and to maintain a thermally stable state, the sample holder is put into the vacuum chamber whose temperature is controlled by the temperature controller between room temperature to 100 °C. Using a lock-in amplifier (SR 810 DSP), the amplitude and phase of 3ω signal voltage were measured through the third harmonic mixer in the lock-in amplifier.

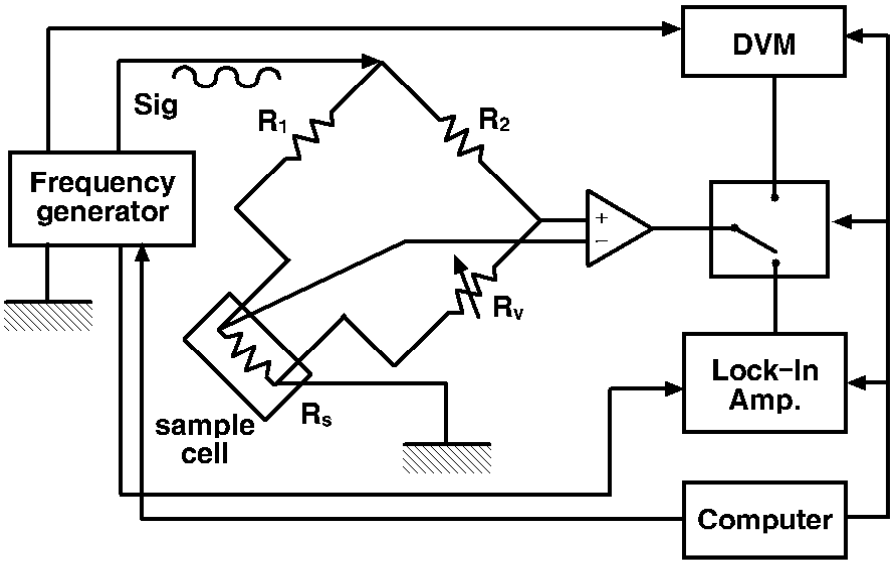


Fig. 4 Schematic of the apparatus for 3ω thermal conductivity measurements.

4. RESULT AND DISCUSSIONS

Fig. 5 shows the transmittance of two film samples measured by the spectrophotometer. The transmittance of the light irradiated sample was reduced more than 10 % and

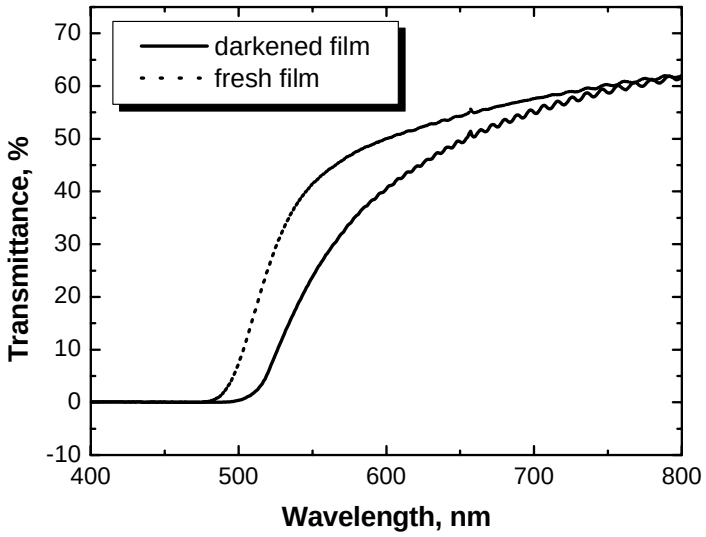
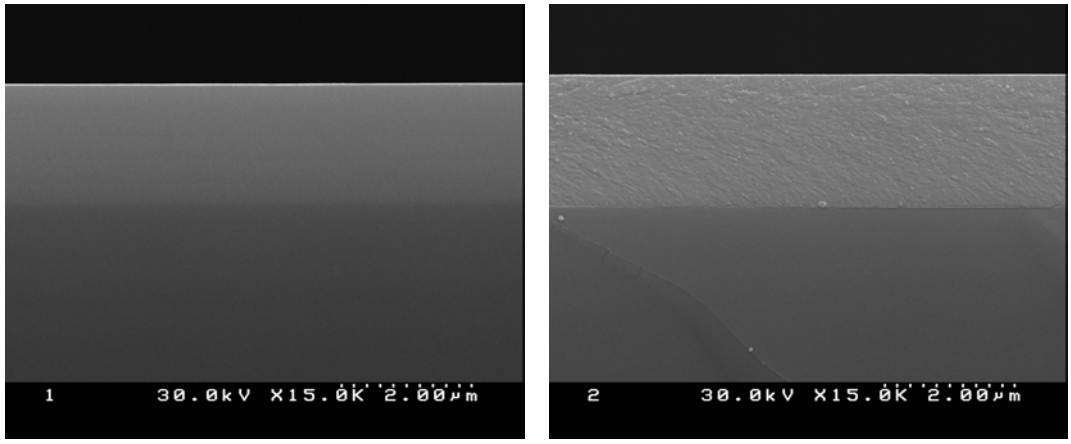
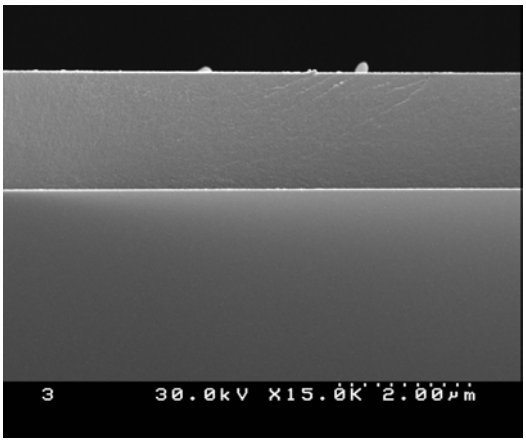


Fig. 5 Transmittance of the fresh and photo-darkened As_2S_3 films measured by spectrophotometer.

shifted toward red wavelength about 40 nm. This means that the normal photo-darkening, accompanied by the red shift of the absorption edge, was induced by the light absorption under the assumption of constant reflectance. It can be checked easily because the irradiated point was darkened.



(a) **(b)**



(c)

Fig. 6 Cross-sectional micrograph of (a) fresh film (b) photo-darkened film (c) annealed films.

Fig. 6 (a),(b), and (c) are the cross-sectional micrograph of a fresh, photo-darkened, and annealed films, respectively. The annealing of the sample was performed at whose glass transition temperature 180 °C for one hour. The grains in fresh film are small and uniform, however the grain size becomes larger by the photo-darkening. After one hour annealing, the collected particles recovered nearly to the fresh film state, however in some points it didn't fully recovered to original state. We think that there are many reasons for this, however the dominant source is the production of As_2O_3 by oxidation in the air [1]. If the film was illuminated in vacuum condition, the film can be restored completely. The stoichiometry and porosity of the film material which affect strongly on the thermal conductivity must be checked for more quantitatively.

In this experiment, it is necessary to know the variation of the resistance of a gold

strip for measurement of the exact thermal conductivity as a function of temperature. During the deposition of the gold strip, the TCR, defined as $\frac{1}{R}\frac{dR}{dT}$, and the resistance could be changed for many other reasons such as an impurity; therefore, we measured and reflected them in our measurement [19].

If we assume that the silicon substrate and As_2S_3 film are thermally one-dimensionally connected, we can obtain the temperature variation of only the thin film by subtracting that of the substrate. In the case of constant amplitude of the heat power per unit length, by substituting this into the right side of Eq. (6), we can obtain the thermal conductivity of thin film. For the case of doped silicon substrate, we cannot neglect the electrical conductivity of the substrate, therefore it is difficult to obtain the accurate TCR of metal line directly. Consequently, we expected the temperature variation of the substrate by the simulation using the known thermal conductivity and diffusivity of silicon. The accuracy of this method was verified through the window glass and it showed that the measured data and simulated data agree well within ± 3% [19].

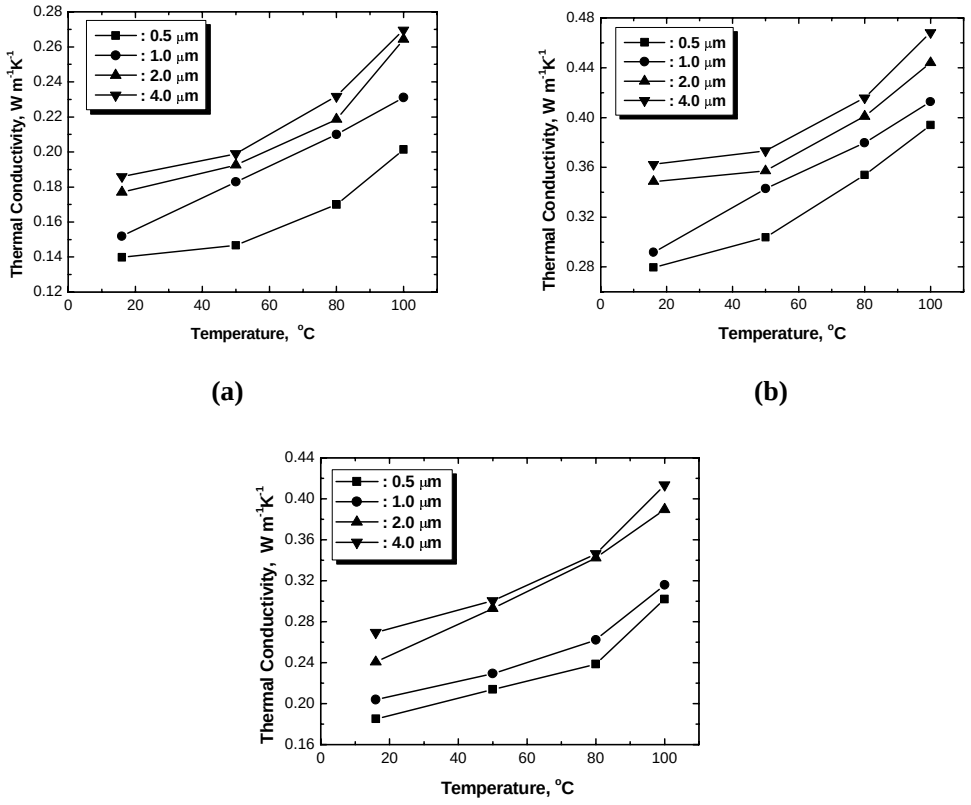


Fig. 7 Experimentally obtained thermal conductivities of (a) fresh films (b) photo-darkened films (c) annealed films.

Fig. 7 (a), (b), and (c) show the obtained thermal conductivities of fresh, darkened, and annealed films, respectively, by 3ω method. In all cases, as the temperature increases, the thermal conductivity also increases and at 100 °C, it becomes nearly twice. This is a common phenomenon in amorphous materials because in such materials, the major heat conduction carrier is phonon and as the temperature increases, its activation energy also increases.

The result shows that thermal conductivities of fresh films were 0.14～0.27 $Wm^{-1}K^{-1}$, however increase to 0.28～0.47 $Wm^{-1}K^{-1}$ after the photo-darkening and decrease to 0.19～0.42 $Wm^{-1}K^{-1}$ after annealing of the sample. These changes can be explained by the change of microstructure produced from the photo-darkening and thermal annealing. As the previous photos in Fig. 6 shows that, the grain size becomes larger during the darkening, however because of the oxidation, it didn't fully return to its original state.

Table I. Experimentally Obtained Thermal Conductivities of As_2S_3 Thin Films.

Temp. (˚C)	Thermal Conductivity ($Wm^{-1}K^{-1}$) x 10^{-1}											
	Fresh Films				Darkened Films				Annealed Films			
	0.5μm	1.0μm	2.0μm	4.0μm	0.5μm	1.0μm	2.0μm	4.0μm	0.5μm	1.0μm	2.0μm	4.0μm
23	1.389	1.518	1.770	1.860	2.795	2.916	3.485	3.625	1.850	2.038	2.406	2.694
50	1.466	1.829	1.926	1.990	3.038	3.428	3.571	3.733	2.137	2.292	2.929	3.004
80	1.699	2.099	2.187	2.318	3.538	3.797	4.010	4.158	2.384	2.621	3.422	3.463
100	2.014	2.311	2.643	2.697	3.937	4.128	4.440	4.684	3.020	3.157	3.895	4.135

This result is comparable to the literature values of several chalcogenide materials whose thermal conductivity is between 0.2~5.0 $Wm^{-1}K^{-1}$ [14,20,21]. The important point is the not the absolute value but the changing rate of the thermal conductivity. Table I shows the obtained data in this experiment.

The result also shows that the thermal conductivity of thicker films are larger than thinner films. This can be explained by the effect from the thermal resistances between the metal strip, film, and the surface of substrate. If we assume that these resistances exist the obtained film thermal conductivity κ_f can be expressed as

$$\kappa_f = \frac{\kappa_i}{1 + R_i \kappa_i / t_f}, \tag{7}$$

where κ_i is the intrinsic thermal conductivity of thin film independent to the thickness of film, and R_i is the total thermal resistance between the layers. From Eq. (7), we can

see that the experimentally obtained thermal conductivity κ_f is always lower than κ_i and thinner films show lower κ_f than thicker film. Actually, because the thermal resistance R_i of the amorphous film is in $2 \sim 4 \times 10^{-8}$ m^2KW^{-1} [22] depending the thickness, the thermal conductivity changes about 20% at maximum. However, the result shows that the changing rate is larger than this, therefore additional investigations will be required.

5. CONCLUSIONS

The thermal conductivities of As_2S_3 films, whose study for thermal properties is insufficient compared to optical, electrical properties, were measured by 3ω method. The fresh, photo-darkened, and annealed As_2S_3 thin film coated on the silicon wafer, whose thicknesses are 0.5μm, 1.0 μm, 2.0 μm, and 4.0 μm, were measured in the range from room temperature to 100 °C. Because thermal resistance between the layers increases, the measured thermal conductivity of thinner films decreases. The result also shows that the thermal conductivities of fresh films were $0.14 \sim 0.27$ $Wm^{-1}K^{-1}$, however increase to $0.28 \sim 0.47$ $Wm^{-1}K^{-1}$ after the illumination of light on the sample and decrease $0.19 \sim 0.42$ $Wm^{-1}K^{-1}$ after annealing of the sample. These can be explained by the change of microstructure produced from the photo-darkening and thermal annealing.

To get more detail mechanism for the change of thermal conductivity, the investigation must be repeated for more wide variety of samples whose illumination time and the stoichiometry of the coated film must be checked. We expect that our experimental results can be the base of application of chalcogenided to imaging, holography and optical memories which utilize the change of thermal properties.

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